U.S. DEPARTMENT OF COMMERCE
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PB-266 312

Improved Procedure for Determining Mercury Emissions from Mercury Cell Chlor-Alkali Plants

Environmental Monitoring & Support Lab, Research Triangle Pk, NC

1976

PB266312

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

SUBJECT: Report(s) for Inclusion in NTIS DATE: May 6, 1977

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1. REPORT NO.	2.	3. PB 266 312
EPA-600/J-76-045	JOURNAL ARTICLE	

4. TITLE AND SUBTITLE	5. REPORT DATE
IMPROVED PROCEDURE FOR DETERMINING MERCURY EMISSIONS FROM MERCURY CELL CHLOR-ALKALI PLANTS	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
W. J. Mitchell and M. R. Midgett	
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Environmental Monitoring and Support Laboratory Quality Assurance Branch, MD-77 Research Triangle Park, North Carolina 27711	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/08

15. SUPPLEMENTARY NOTES

REFERENCE: APCA JOURNAL, Vol. 26, No. 7, 675-677, July 1976

16. ABSTRACT

An analytical procedure for determining the mercury emissions from mercury cell-chlor-alkali plants is described. This procedure was developed to correct problems in an analytical procedure promulgated by the Environmental Protection Agency. This improved analytical procedure was subjected to a collaborative test in which 13 laboratories performed duplicate analyses on 3 solutions that contained mercury concentrations in the range of 2 to 65 micrograms of mercury per milliliter. From this collaborative test the following estimates are made about the precision and accuracy of the improved procedure: the within-laboratory standard deviation is 1.6 μg Hg/ml, the between-laboratory standard deviation is 1.8 μg Hg/ml, and the accuracy is -0.4 μg Hg/ml.

micrograms

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	6
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	A02-A01

EPA Form 2220-1 (9-73)

EPA-600/J-76-045
JOURNAL ARTICLE

Improved Procedure for Determining Mercury Emissions from Mercury Cell Chlor-Alkali Plants

W. J. Mitchell and M. R. Midgett
U. S. Environmental Protection Agency

An analytical procedure for determining the mercury emissions from mercury cell chlor-alkali plants is described. This procedure was developed to correct problems in an analytical procedure promulgated by the Environmental Protection Agency. This improved analytical procedure was subjected to a collaborative test in which 13 laboratories performed duplicate analyses on 3 solutions that contained mercury concentrations in the range of 2 to 65 micrograms of mercury per milliliter. From this collaborative test the following estimates are made about the precision and accuracy of the improved procedure: the within-laboratory standard deviation is 1.6 μg Hg/ml, the between-laboratory standard deviation is 1.8 μg Hg/ml, and the accuracy is −0.4 μg Hg/ml.

Elemental mercury is the primary pollutant emitted to the atmosphere by mercury cell chlor-alkali plants. To ensure that the ambient air concentration of mercury in the vicinity of these plants does not exceed 1 microgram per cubic meter ($\mu g/m^3$) of air, U. S. Environmental Protection Agency (EPA) regulations limit the mercury emissions from these plants into the atmosphere to 2300 grams per day.[1] These regulations require that the mercury emissions be measured by collecting them in an acidic 0.1M iodine monochloride solution (ICl) and then analyzing the samples using the following cold vapor atomic absorption procedure: 1. an aliquot from the collected sample is diluted to 50 ml using 0.1M ICl, 2. the solution is made basic using NaOH and shaken vigorously, 3. 5 ml of hydroxylamine sulfate—a reducing agent that converts the mercury(II) ion to elemental mercury—is added, 4. the solution is shaken and then immediately placed in the aeration system, and 5. the elemental mercury formed is flushed from the solution using an air stream and passed through the optical cell of an atomic absorption spectrophotometer where its absorption at 253.7 nanometers (nm) is determined.

When the above test method was subjected to a collaborative test, the analytical procedure was found to give both imprecise and inaccurate results.[2] From interviews with the test participants and a statistical analysis of the data the following problems were identified in the analytical procedure: nonreproducible blanks; sudden shifts in the calibration curve; formation of a black precipitate when the 10N NaOH was added; loss of elemental mercury from the aeration bottle before it could be inserted in the aeration system; and lack of specific instructions about how to construct the aeration system, what materials to use, and the amount of dilution needed to bring the source samples into the working range of the procedure.

Subsequently, we initiated work to modify and improve the procedure and still keep it compatible with the use of ICl as the absorbing reagent for mercury. This constraint was necessary for three reasons: 1. in all the sampling done for the purpose of setting the standard, ICl was used as the collecting liquid; 2. the ICl was known to quantitatively collect both elemental mercury and mercury compounds; and 3. solid type collectors for mercury[3-5] were inadequate for handling the large quantities of mercury (50 mg) and the high sampling rates (25 lpm) associated with source sampling for mercury. Thus, the scope of this study was limited to identifying the causes of error in the analytical procedure and modifying the procedure to eliminate these sources of error.

This investigation resulted in the development of the analytical procedure described below. This procedure was de-

veloped for use on any atomic absorption spectrophotometer, that has an open sample presentation area in which to mount the aeration cell-optical assembly described below.

Experimental Parameters Studied

Iodine monochloride was found to be the cause of both the nonreproducible blank and the sudden calibration shifts. Diluting the samples in an aqueous 5% H_2SO_4 solution instead of 0.1M ICl solved this problem and also removed the need to neutralize the sample with 10N NaOH before analysis.

One cause of imprecision in all analytical procedures that use aeration of elemental mercury from solution is the loss of mercury after the reducing agent is added, but before the aeration bottle is attached to the aeration system. To remove this source of error an aeration cell-optical cell combination (Figures 1 and 2) was developed to allow the reducing agent to be added after the aeration cell was attached to the aeration system (Figure 3). (In constructing this aeration cell the use of a glass frit was avoided because previous experience had shown that the frit was a major source of cross contamination between samples.)

Another general problem with these methods is the condensation of water and mercury in the aeration system. To prevent this, some procedures recommend the use of a drying tube[6] but we found that the tubes must be replaced after 8 to 10 samples and the system must then be reconditioned and recalibrated. Others[3,4] wrap heating wire around the system and heat to a high temperature (95°C)—an improvement over the drying tube approach. However, we found that if the heating wire is covered with asbestos tape (Figure 2) good precision is obtained when the system is only heated to 5°C above ambient temperature.

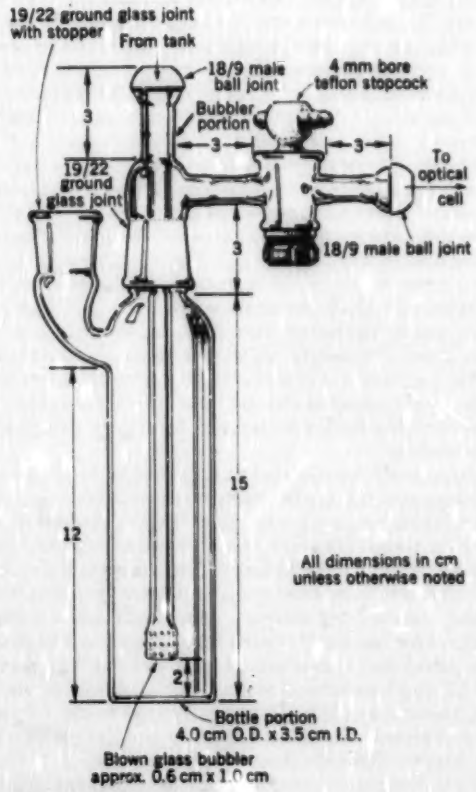

Figure 1. Aeration cell.

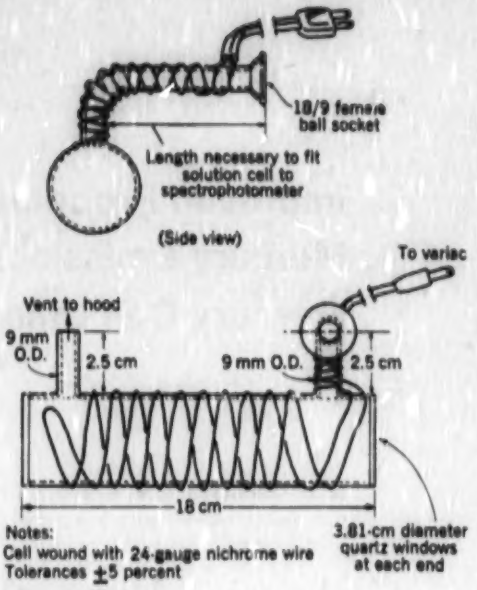

Figure 2. Optical cell.

After these modifications were made to the original procedure, we evaluated the effect of the following variables on the accuracy and precision of the modified procedure: the maximum ICl concentration that could be tolerated; the reducing agent employed; the minimum time required between addition of the reducing agent and initiation of aeration; the need to stir the solution after the addition of the reducing agent, the flow rate of the aeration gas, and the linear range of the absorption curve. It was found that: release of mercury is complete as long as the ICl concentration in the aeration cell does not exceed 1×10^{-4} M; tin(II) ion is the only suitable reducing agent when the samples are diluted in the aqueous sulfuric acid solution; at least 15 sec should be allowed for reduction of the mercury before aeration is initiated; stirring the sample after the addition of the reducing agent and before and during aeration gives sharper and more reproducible peak maxima; the sharpest peak maximum is obtained with the aeration gas flowing through the system at 1.5 lpm; and under the above conditions, the absorbance is linear when the aeration cell contains less than 1100 ng of mercury.

The Improved Analytical Procedure

Reagents

Tin(II) Chloride (crystal). Any brand of tin(II) chloride that will give a clear solution when dissolved as described below can be used. (Tin(II) sulfate is an acceptable substitute

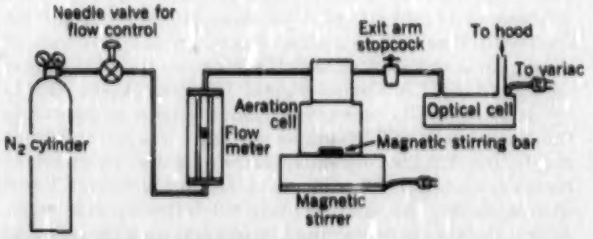

Figure 3. Schematic of the aeration system.

provided it yields a clear solution.) Prepare this reagent fresh daily and keep it sealed when not being used. It should be prepared by dissolving 20 g of $SnCl_2$ or 25 g of $SnSO_4$ in 25 ml of concentrated HCl and then diluting this solution to 250 ml with distilled water.

Mercury(II) Stock Solution. (1 mg Hg/ml). Prepare the solution in a 100 ml volumetric flask as follows: completely dissolve 135.4 mg of ACS Reagent Grade $HgCl_2$ in 75 ml of distilled water, add 10 ml of concentrated HNO_3, and adjust the volume to 100 ml with distilled water. Mix thoroughly. (This solution should be stable for at least 1 month.)

Intermediate Mercury Standard Solution. (10 μg Hg/ml.) Prepare a fresh solution each week by pipetting a 5.0-ml aliquot of the Hg stock solution into a 500 ml volumetric flask and adding 20 ml of the 5% H_2SO_4 solution. Adjust the volume to 500-ml using distilled water. Mix thoroughly.

Working Mercury Standard Solution. (200 ng Hg/ml.) Prepare the solution fresh daily by pipetting a 5.0 ml aliquot from the Intermediate Mercury Standard Solution into a 250 ml volumetric flask. Add 10 ml of the 5% H_2SO_4 solution and 2 ml of the 0.1M ICl that was prepared for sample collection, dilute to 250 ml with distilled water and mix thoroughly.

Equipment Calibration

Optical Cell Heating System Calibration. Using a 50 ml graduated cylinder, add 50 ml of distilled water to the bottle section of the aeration cell and attach the bottle section to the bubbler section of the cell. Attach the assembled aeration cell to the optical cell and, while aerating at 1.5 lpm, determine the minimum Variac setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing.

Spectrophotometer Calibration. Set the spectrophotometer wavelength dial to 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent condensation from occurring. Then set the recorder full scale as follows: use a 50 ml graduated cylinder to add 50 ml of distilled water to the aeration cell bottle and pipet a 5.0 ml aliquot of the working Hg standard solution into the aeration cell. (Note: The Hg-containing solution should always be added to the aeration cell after the 50 ml of distilled water.) Place a Teflon coated stirring bar in the bottle. Before attaching the bottle section to the bubbler section of the aeration cell, make certain that the aeration cell exit arm stopcock (Figure 1) is closed, and there is no flow through the bubbler. Now attach the bottle section to the bubbler section of the aeration cell.

Pipet 5.0-ml of the $SnCl_2$ solution into the aeration cell through the sidearm of the cell and immediately stopper the sidearm. Stir the solution for 15 sec, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90% of the recorder full scale.

To prevent Hg carry-over from one sample to another, it is important that the nitrogen tank valve be closed and the aeration cell disconnected from the optical cell only after the recorder pen has returned to the baseline. (It should not be necessary to disconnect the aeration gas inlet line from the aeration cell when changing samples.) After separating the bottle and bubbler sections of the aeration cell, place the bubbler section into a 600 ml beaker containing approximately 400 ml of distilled water and rinse the bottle section of the aeration cell with a stream of distilled water. (Usually this washing is all that is necessary to remove all traces of the reducing agent, but it will be necessary to wash the aeration cell parts with concentrated HCl if any of the following conditions occur: a white film appears on any inside surface of the solution cell, a sudden change is observed in the calibration curve, or repeatable results are not obtained on replicate samples.)

Repeat the above procedure with successive 5.0 ml aliquots of the working mercury standard solution until two consecutive peak heights agree within 3% of their average value—generally this will require a maximum of three replicates. Similarly, determine the absorbance maxima of standards prepared by taking 0.0 ml (blank), 1.0 ml, 2.0 ml, 3.0 ml, and 4.0 ml aliquots of the working standard solution. The final amount of mercury in the aeration cell for the 0.0 ml, 1.0 ml, 2.0 ml, 3.0 ml, 4.0 ml, and 5.0 ml aliquots will be 0.0, 200, 400, 600, 800, and 1000 ng, respectively.

Determine the peak maxima for each standard and subtract the average peak height of the blank (0.0-ml aliquot), which should be less than 2 percent of recorder full-scale, from the averaged peak heights of each standard. Plot the corrected peak height of each standard versus the corresponding final mercury concentration in the aeration cell (in nanograms) and draw the best fit straight line. If the plot does not pass through or lie very near to the origin, check for non-linearity of the curve and for incorrectly prepared standards.

Dilution and Analysis of the Samples

Pour the contents of the sampling train into a 1000 ml flask and adjust the volume to 1000 ml with distilled water. Pipet a 2.0 ml aliquot of this solution into a 250 ml volumetric flask. Add 10 ml of the 5% H_2SO_4 solution and adjust the volume to 250 ml with distilled water. This solution should be stable for at least 72 hours.

Repeat this entire dilution procedure for each Hg source test sample. (As written, this dilution should bring source samples that contain between 0.5 and 120 μg Hg/ml, after dilution to 1000 ml, into the working range of the analytical procedure. By suitable dilution samples containing in excess of 120 μg Hg/ml can be analyzed by this method, but because iodine monochloride may interfere with the reducing agent, source samples originally containing less than 0.5 μg Hg/ml should not be analyzed by this method.)

After calibrating the spectrophotometer as described above, add 50 ml of distilled water to the aeration cell bottle and then pipet 2.0 ml of the diluted Hg source test sample into the aeration cell bottle and perform the procedure used to establish the calibration curve. Analyze successive aliquots of each source sample until two consecutive peak heights agree within ±3% of their average value.

Note: If the peak maximum of a sample is less than 10% of the recorder full-scale, a larger aliquot of the diluted sample—not to exceed 5.0 ml can be used. If the peak maximum of a sample is off-scale, further dilution of the original source sample should be done to bring the mercury concentration into the linear range of the procedure.

Calculations

For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within ±3% for the contribution of the blank. Use the spectrophotometer calibration curve and this corrected average to determine the final Hg concentration in the aeration cell for each source sample, $[Hg]_{a.c.}$. Then, calculate the mercury concentration in milligrams in the source sample, $(Hg)_0$, using Equation 1.

$$(Hg)_0 = [Hg]_{a.c.}(D.F.)\left(\frac{1}{s}\right)(V)\left(\frac{1\ mg}{1000\ ng}\right) \qquad (1)$$

Table I. Collaborative test results in μg Hg/ml for the revised FAA Procedure for Mercury.

Sample No.	Laboratories													Mean
	101	102	103	104	105	106	107	108	109	110	111	112	113	
1[a]	24.5	25.5	24.0	22.0	23.6	151.0[b]	24.0	26.5	21.8	25.0	22.1	21.4	21.4	23.53
	23.5	25.5	24.3	23.5	24.1	21.6[b]	24.0	24.9	21.8	25.0	22.1	22.4	22.5	
2[a]	2.5	3.0	2.9	3.3	3.0	1.1	3.2	3.1	2.8	3.5	3.6	2.5	2.5	2.66
	1.0	2.5	2.9	3.3	3.2	0.9	3.0	3.9	2.8	1.5	3.3	2.5	2.5	
3[c]	64.0	67.5	64.0	62.0	63.9	60.1	63.0	64.6	62.0	60.0	61.6	62.0	62.0	63.71
	67.5	68.5	64.8	63.5	63.9	60.8	63.0	76.2	62.3	60.0	63.4	62.0	62.0	

[a] Source sample from a mercury cell chlor-alkali plant.
[b] Results not used in estimating the precision and accuracy of the analytical procedure.
[c] Laboratory-prepared mercury(II)chloride solution that contained 64.3 μg Hg/ml (based on a NAA analysis).

where:

$(Hg)_0$ = Total concentration of mercury (in milligrams) in the source sample after dilution to 1 liter.
$[Hg]_{s.c.}$ = Total concentration of mercury (in nanograms) in the aeration cell (obtained from the calibration curve).
D.F. = Total dilution factor for the mercury sample before addition to the aeration cell. For example (250 ml/2 ml) would be the dilution factor if the source samples were diluted as described in the Dilution and Analysis Section above.
a = Aliquots size (in milliliters) added to the aeration cell.
V = 1000 ml

Collaborative Test

Thirteen independent laboratories, which are referenced in this report as Laboratories 101, 102, etc., participated in the collaborative test. Five of these laboratories were EPA Regional laboratories, seven were associated with mercury cell chlor-alkali plants, and the last was a commercial laboratory. Two source samples from a mercury cell chlor-alkali plant were used in the collaborative test. Each sample was diluted to 1 liter with distilled water and then subdivided and distributed among the 13 participating laboratories so that each laboratory received two separate aliquots of each sample. Likewise, a $HgCl_2$ standard solution—prepared by dissolving 87.08 mg of $HgCl_2$ in 500 ml of 0.1 M ICl and then diluting to 1000 ml with distilled water—was also distributed so that each laboratory received two separate aliquots of this solution. However, because the six individual aliquots received by each laboratory were identified by different numbers, the 13 participating laboratories were not aware that they had received three sets of duplicate samples but rather thought they had received six different samples.

The results of the collaborative test are presented in Table I. Since the laboratory error variance was homogeneous and constant across concentration levels, the results from all 13 laboratories were pooled (with the exception of sample 1, Laboratory 106) to obtain the following estimates of the precision and accuracy of the analytical procedure over the concentration range of 2 to 65 μg Hg/ml:

Within-laboratory standard deviation. The estimated within-laboratory standard deviation of the procedure for a sample that has been diluted and analyzed in duplicate in the same laboratory is 1.6 μg Hg/ml.

Between-laboratory standard deviation. The estimated between-laboratory standard deviation of the procedure for a sample that has been diluted and analyzed in duplicate in two different laboratories is 1.8 μg Hg/ml.

Accuracy. The estimated accuracy of the procedure, which is based on the analysis of a mercury standard that contained 64.3 μg Hg/ml, is −0.4 μg Hg/ml.

Acknowledgments

The authors wish to thank the following individuals, who participated in the collaborative test: L. V. Haff of Allied Chemical Corp., Solvay, NY; L. E. Tufts of Hooker Specialty Chemicals Division, Niagara Falls, NY; M. E. Webb of Monsanto Industrial Chemicals Co., Sauget, IL; A. McDowell of Dow Chemical of Canada, Ltd, Sarnia, Ontario; T. P. Broad of Olin Chemicals Corp., Niagara Falls, NY; R. Shepard of Diamond Shamrock Corp., Painesville, OH; W. Fall of Stauffer Chemical Co., Dobbs Ferry, NY; A. Compton of Tradet, Inc., Columbus, OH; A. Clark of EPA-Region I, Needham Heights, MA; L. Kahn of EPA-Region II, Edison, NY; R. Miller of EPS-Region V, Chicago, IL; J. Robinson of EPA-Region VII, Kansas City, KA; and A. Gahler of EPA-Region X, Seattle, WA.

J. C. Suggs, Dr. J. E. Knoll, and J. P. Lambert of EPA, Research Triangle Park, NC are also thanked for their assistance in this study.

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